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Field Study of Carbon Monoxide and Light Hydrocarbon Production Related to Natural Biological Processes

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Several field experiments were conducted to determine whether a correlation exists between marine biological standing stocks and the production of carbon monoxide and light hydrocarbons. Earlier laboratory experiments using bacteria-free cultures definitely established a relation between biological organisms and gas production. A field sampling program was established at Miami, Fla., and two sites were selected, one in the Gulf Stream and the other near shore. Several samples were obtained over a

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period beginning in February 1972 and ending in June 1972. There appears to be a direct correlation between several of the parameters, notably total algal population, chlorophyll a, and primary productivity, all of which relate to carbon monoxide and hydrocarbon gas production. The correlation is very evident for the near-shore station and less pronounced in the Gulf Stream, where biological productivity is considerably lower.

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FIELD STUDY OF CARBON MONOXIDE AND LIGHT HYDROCARBON PRODUCTION RELATED TO NATURAL BIOLOGICAL PROCESSES

INTRODUCTION

Several field experiments were conducted to determine whether a correlation exists between marine biological standing stocks and the production of carbon monoxide and light hydrocarbons. The reported results are preliminary, and additional investigations are required.

In previous field experiments, vertical distributions of gaseous hydrocarbons, C_1 to C_4, and carbon monoxide have been determined for various oceanic areas [1-5]. However, no biological measurements were obtained on the samples. In the surface waters of the open ocean, methane appears to be in near equilibrium with the atmospheric concentration. In coastal and certain anoxic areas, methane is usually supersaturated relative to the atmosphere [6, 7]. On the other hand, carbon monoxide in the open oceans is highly supersaturated. The CO concentration also exhibits a well-defined diurnal cycle suggesting the influence of photochemical and biological processes [4].

Insufficient solubility coefficient data are available to determine the degree of saturation in natural seawater for C_2 to C_4 hydrocarbons. Several observations have been made concerning the distribution of these light hydrocarbons. In the upper layer (0-150 m) of the oceans, olefins generally have been found to be higher in concentration than their saturated homologs [1, 2], and they also show pronounced peaks in this region. This nonhomogenous distribution suggests the existence of processes occurring at rates faster than physical mixing. It also suggests a possible correlation between these gases and biological processes. Unfortunately, in this early work on hydrocarbons and CO, no supporting biological data were available for comparison.

Controlled laboratory experiments were devised to explain the role of living algae and their by-products in the production of CO and hydrocarbons [8]. These experiments identified and measured carbon monoxide and hydrocarbons released by bacteria-free cultures of the ultradiation *Chaetoceros galvestonensis* growing under cool white fluorescent lamps. Sterile controls were made with natural seawater to which nutrients were added. These control samples were incubated in the same light and also showed production of CO and unsaturated hydrocarbons, but at rates much lower than in samples that had supported algal growth. The production of CO and light hydrocarbons was also found to be directly related to the amount of dissolved organic carbon (DOC) present in the natural seawater sample. Four general observations are listed relating to the laboratory experiments:

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1. All samples (blank seawater, seawater with DOC secreted by the organism, and seawater containing viable algal cells) produced varying amounts of gaseous products.

2. The predominant hydrocarbon gases produced were carbon monoxide, ethylene, propylene, and butenes, with smaller amounts of ethane and propane detectable. For a given light intensity and time of exposure, the amounts of gaseous products in the seawater containing the organism were always higher than in the blank seawater.

3. Only trace amounts of methane were produced in the cultures.

4. No hydrocarbon gases were found, and only a slight production of carbon monodixe took place in samples incubated in the dark. These laboratory experiments definitely established a relation between biological activity and the production of hydrocarbon and CO gases. The mechanisms accounting for these gaseous products remain to be defined.

METHODS AND FIELD SITES

Several criteria were set forth in selecting the site for the field experiment. The sampling site should be conveniently accessible by small boat. The location should be within 1 h boat travel of a shore-based laboratory. This would allow one sampling period in the morning, with analysis of the samples before an afternoon sampling trip. It was also desirable to collect water from two distinctly different water masses, and that one of the two sampling sites be biologically highly active with respect to the other. Anthropogenic contamination (sewage and oil spills) should be avoided at both locations.

With these criteria in mind, two sites were finally selected (Fig. 1). One was oligotrophic in nature and located in the Gulf Stream off Miami, Florida; the other was a nearby in-shore location in a basically different water region. The Gulf Stream sampling station was in 150 m of water about 16 km (10 mi) east of Bear Cut, which separates Virginia Key from Key Biscayne. The near-shore station was located in 10-15 m of water about 5.4 km (3 mi) east of Key Biscayne, also near Bear Cut. After preliminary tests, the first meaningful samples were obtained on Feb. 8, 1972. Samples were collected at 2-week intervals beginning with that date and extending to June 13, 1972. No bloom of any magnitude occurred during this period. Weather conditions during the sampling period were usually sunny with moderate seas (1 m). Roughest conditions were encountered during sampling on Mar. 21, 1972, with partly overcast skies and 2- to 5-m seas. There were no sampling days with total overcast.

Samples were collected in 12-l Niskin bottles. Morning samples were taken at 1000 h and afternoon samples at 1500 h, weather permitting. Of the ten sampling days, no morning samples and only three afternoon samples were missed. Samples were analyzed within 2 h of collection. All samples collected for hydrocarbon gas analysis were treated with a respiratory inhibitor, sodium azide, at the time of collection to stop all metabolic activity. The dissolved gas analysis for CO and light hydrocarbons in these samples was performed by a gas chromatographic method. The technique has been described elsewhere [9, 10]. The samples were analyzed for methane, ethane, ethylene, propane, butane, butenes, and carbon monoxide. The analysis for oxygen was made by the standard Winkler method. Other measurements made on the same seawater samples were

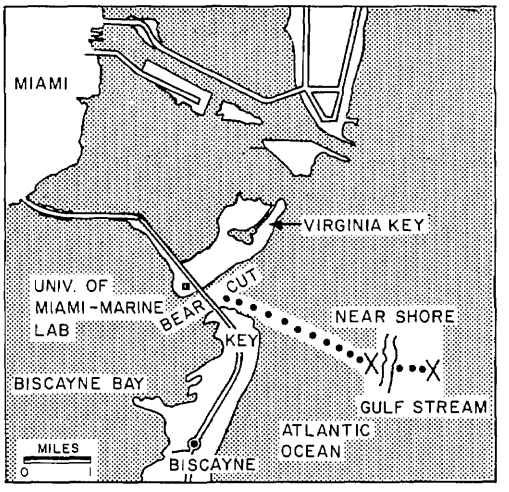

Fig. 1—Map showing laboratory and sampling sites

temperature, salinity, chlorophyll a, DOC, particulate carbon, nitrate, ammonia, algal population density, and light-box primary productivity. The analytical procedures for the above measurements follow Strickland and Parsons [11].

All surface water data for the above measurements, both in the Gulf Stream and near shore, are reported in Tables 1 and 2 respectively. These tables list the various parameters that were measured, the concentration units for these parameters, and the results of each day's sampling. The reported concentrations are the average of the morning and afternoon samples. The last line in Table 1 and the next to last line in Table 2 give the average concentrations of the various parameters during the ten sampling periods from Feb. to June, 1972. The last line in Table 2 shows the ratio of the NPAR-Shore average concentrations to the Gulf Stream average concentrations. In both tables, the number of centric and pennate diatoms, as well as the total number of cells are, for convenience, reported as the log of the number. In the figures, however, the actual numbers of cell counts were plotted. Figures 2 and 3 are graphs of the data reported in Tables 1 and 2.

RESULTS AND DISCUSSION

Plotted along the abscissa of Figs. 2 and 3 are the sampling days, starting with Feb. 8, 1972, and concluding with June 13, 1972. The abscissa is further divided into Gulf Stream station on the left side and near-shore station on the right side. Plotted on the ordinate are the measured concentrations of oxygen, CO, and the hydrocarbons. Also plotted are the other chemical and biological parameters reported in Tables 1 and 2. It is apparent from a visual inspection of the Gulf Stream station, Figs. 2 and 3, that there was very little change in hydrocarbon and CO concentrations during the 6-month experiment. The only significant concentration changes observed for the Gulf Stream were peaks of particulate carbon observed on Mar. 21, 1972, and May 2, 1972. There was also

Table 1—Experimental Data for Gulf Stream Station: Surface Water (1972)*

Date of Samples	Parameters at Gulf Stream Station																	
	Methane (10^{-6}ml/l)	CO (10^{-6}ml/l)	Ethane (10^{-6}ml/l)	Ethylene (10^{-6}ml/l)	Propane (10^{-6}ml/l)	Propylene 10^{-6}ml/l	DOC (mg-C/l)	Chloro-phyll a (μg/l)	Particulate Carbon (mg-C/m^3)	Fixation Rate Carbon (mg-C/m^3/h)	Oxygen (ml/l)	Salinity ‰	Temperature (°C)	Ammonia (μg-at N/l)	Nitrate (μg-at N/l)	Log Total Cells (cells/21)	Log Centric Diatoms (cells/21)	Log Pennate Diatoms (cells/21)
2-8-72	57	—	0.7	4.2	0.9	1.2	1.17	0.19	227	0.87	5.09	35.32	25.0	0.74	0.18	—	—	—
2-22-72	61	21	0.7	2.8	1.2	0.7	1.28	0.15	182	0.03	5.04	35.85	24.5	0.87	0.30	3.513	3.121	3.100
3-7-72	47	33	0.7	4.5	0.5	1.3	1.39	0.09	230	—	5.24	35.86	25.0	0.81	0.22	3.789	3.000	3.270
3-21-72	49	31	0.5	3.7	0.5	0.9	1.43	0.21	580	—	5.21	36.18	24.3	0.86	0.15	3.899	3.070	2.976
4-4-72	52	46	0.7	4.1	1.1	1.2	1.43	0.18	277	0.05	5.27	36.15	25.0	1.78	0.21	4.209	3.840	3.716
4-18-72	44	28	0.2	3.7	0.8	1.2	1.56	0.11	198	0.04	5.15	36.13	26.4	1.62	0.53	4.151	3.304	3.606
5-2-72	54	50	0.6	4.8	0.6	1.2	1.44	0.37	285	0.29	5.24	36.20	26.5	0.02	0.23	4.754	4.003	4.423
5-16-72	56	86	0.4	7.7	0.3	2.1	1.48	0.25	180	0.03	5.45	36.28	28.0	1.50	0.21	4.634	3.675	4.285
5-30-72	119	92	1.0	16.1	0.8	3.8	0.42	0.37	150	0.24	5.64	36.00	27.0	1.60	0.20	5.381	5.015	4.808
6-13-72	51	32	0.6	8.2	0.4	1.5	—	0.29	115	0.12	5.36	36.11	27.9	1.40	0.30	4.562	3.760	4.135
Average†	59	47	0.6	6.0	0.7	1.5	1.34	0.22	240	0.17	5.27	35.98	26.0	1.20	0.25	41 650‡	15 170‡	15 450‡

*Average of morning and afternoon samples.
†Average concentration over a 6-month period.
‡Actual number of cells.

Table 2—Experimental Data for Near-Shore Station: Surface Water (1972)*

Date of Samples	Parameters at Near-Shore Station																	
	Methane (10^{-6}ml/l)	CO (10^{-6}ml/l)	Ethane (10^{-6}ml/l)	Ethylene (10^{-6}ml/l)	Propane (10^{-6}ml/l)	Propylene (10^{-6}ml/l)	DOC (mg-C/l)	Chloro-phyll a (μg/l)	Particulate Carbon (mg-C/m^3)	Fixation Rate Carbon (mg-C/m^3/h)	Oxygen (ml/l)	Salinity ‰	Temperature (°C)	Ammonia (μg-at N/l)	Nitrate (μg-at N/l)	Log Total Cells (cells/2l)	Log Centric Diatoms (cells/2l)	Log Pennate Diatoms (cells/2l)
2-8-72	77	—	0.8	5.5	1.2	1.9	1.31	0.26	196	0.15	5.07	34.40	24.5	1.04	0.17	—	—	—
2-22-72	75	61	0.8	4.0	0.6	1.1	1.13	0.32	129	0.34	5.15	34.64	22.5	0.64	0.24	3.917	3.079	3.749
3-7-72	82	93	1.0	8.4	0.7	3.0	1.29	0.50	182	—	5.30	34.43	233	2.30	0.25	4.624	3.255	4.360
3-21-72	372	86	3.0	233	1.2	7.9	1.39	2.39	650	1.28	5.39	35.09	23.6	1.57	0.73	6.228	6.164	5.334
4-4-72	184	64	1.2	10.0	1.1	3.2	1.27	0.56	350	0.30	5.51	35.05	23.9	1.85	0.21	4.905	4.349	4.579
4-18-72	149	100	0.5	17.1	0.9	3.4	1.41	0.17	240	0.114	5.35	34.8	26.6	0.77	0.24	4.653	3.487	4.193
5-2-72	285	351	3.0	24.0	1.1	7.6	1.28	1.24	400	0.55	5.31	34.70	25.3	0.74	0.19	6.085	5.706	5.815
5-16-72	111	77	0.5	13.0	0.4	3.5	1.30	0.27	200	0.05	5.41	34.69	28.3	2.3	0.22	4.738	3.647	4.608
5-30-72	357	199	2.8	38.4	1.4	10.8	1.22	0.36	126	0.44	5.64	35.00	27.5	1.30	0.20	5.575	5.191	5.303
6-13-72	168	45	1.2	17.0	0.8	4.2	—	1.0	173	0.89	5.33	34.80	27.6	1.2	0.22	5.945	5.431	5.729
Average†	186	120	1.5	16.1	0.94	4.7	1.29	0.71	256	0.46	5.35	34.77	25.3	1.37	0.27	568 800§	269 000§	126 700§
R‡	3.15	2.55	2.46	2.68	1.32	3.11	0.96	3.22	1.06	2.71	1.02	0.97	0.97	1.16	1.08	13.7	17.8	8.2

*Average of morning and afternoon samples.
†Average concentration over a 6-month period.
‡Ratio of near-shore average to Gulf Stream average (concentration factor).
§Actual number of cells.

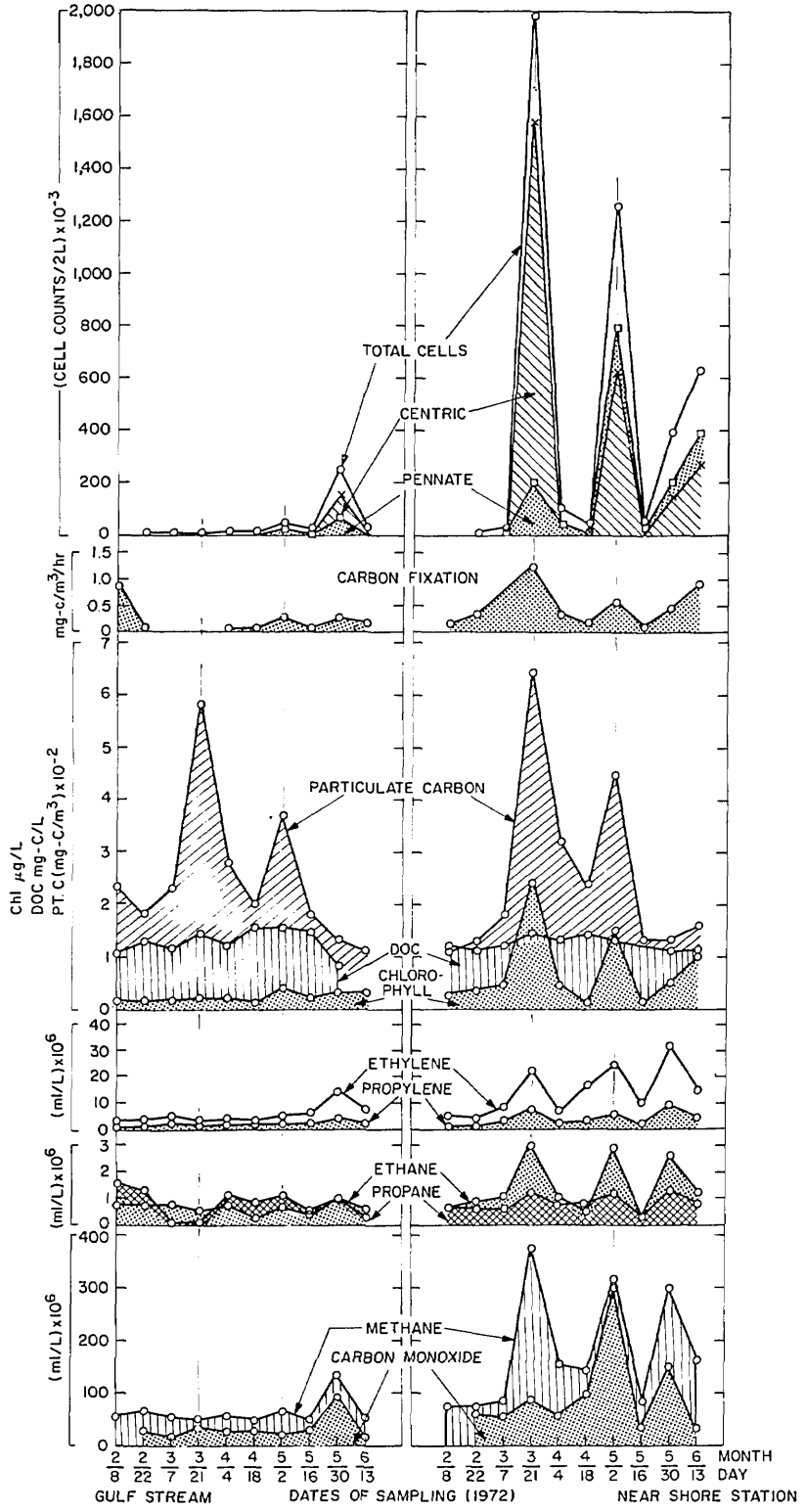

Fig. 2—Comparison of chemical and biological parameters for two ocean stations in the vicinity of Miami, Fla. Left side of figure corresponds to Gulf Stream station, right side to near-shore station.

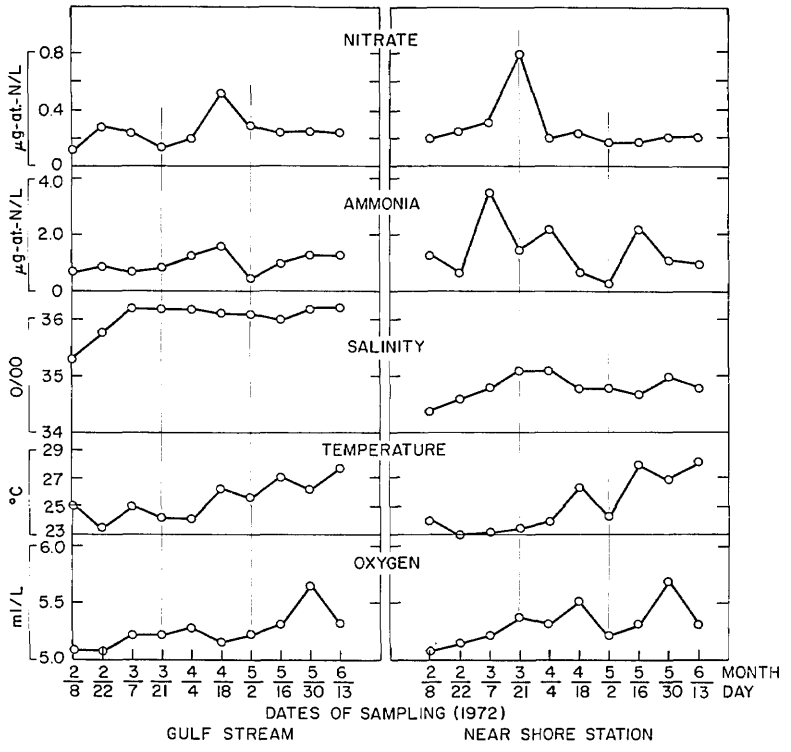

Fig. 3—Comparison of chemical and physical parameters for two ocean stations in the vicinity of Miami, Fla. Left side of figure corresponds to Gulf Stream station, right side to near-shore station.

an increase in cell numbers on May 30, 1972. ^{14}Carbon fixation rates and chlorophyll a parameters were very low during the entire sampling period. Comparing the chemical data of Fig. 3 and the biological and chemical data of Fig. 2 with the hydrocarbon and CO data of Fig. 2, shows that biological processes and the production of gases for the Gulf Stream are relatively low. There was an apparent increase in hydrocarbon concentration observed on the May 30, 1972, sampling period. This may be related to the slight cell increase for that period, during which oxygen also exhibited a slight increase.

It appears that of the parameters recorded, the production of hydrocarbons and carbon monoxide was most closely related to the number of phytoplankton cells present in the seawater. This agrees generally with findings involving laboratory experiments with pure bacteria-free cultures of algae [8]. The other parameters such as chlorophyll, DOC and ^{14}carbon fixation rate, had little or no evident influence on gas production. They may, however, contribute to the hydrocarbon and carbon monoxide baseline concentrations.

Comparing the Gulf Stream and near-shore stations (Figs. 2 and 3) shows considerable changes in hydrocarbon concentrations and corresponding changes in some of the routine biological parameters. Visual inspection of the near-shore data reveals very obvious peaks. The numbers of algal cells were orders of magnitude higher than in the Gulf Stream. Two distinct concentration peaks occurred on Mar. 21, 1972, and May 2, 1972.

The carbon fixation data at the near-shore station remained relatively low; however, there was evidence of activity peaks corresponding to algal population peaks. Particulate carbon at the near-shore station exhibited concentration peaks similar in magnitude and time to those observed for the Gulf Stream, although the Gulf Stream peaks were not associated with phytoplankton increases. The DOC concentration at the near-shore station was commensurate with the concentration levels found in the Gulf Stream. No DOC concentration peaks are observed for either near-shore or Gulf Stream stations. The near-shore chlorophyll a concentrations exhibited peaks that correspond to those of the cell counts, the productivity, and the particulate carbon. The other measured parameters of the near-shore station (nitrate, ammonia, temperature, and oxygen) did not exhibit concentration peaks at the times observed for the peak biological parameters.

The unsaturated hydrocarbons, particularly ethylene, show concentration peaks that, in general, correspond with the biological parameters. The saturated hydrocarbons and methane also tend to demonstrate this relationship. Carbon monoxide concentration peaks for the most part agree reasonably well with the hydrocarbon and biological peaks. The one obvious deviation from this agreement is the near-shore carbon monoxide sample of Mar. 21, 1972. We have no logical argument to explain this departure from the general situation. It appears that the production of hydrocarbons and carbon monoxide is most influenced by the number of cells present. This is clearly evident for the near-shore station. In the Gulf Stream, the only increase in cell counts observed (May 30, 1972) was accompanied by a slight increase in hydrocarbon and carbon monoxide.

The concentration factor R reported in Table 2 covers a range from 0.96 for the DOC to 17.8 for centric diatom cells. A factor of near 1 simply means that there is little or no difference in the average concentration for that parameter between the Gulf Stream and near-shore stations. There is virtually no difference between the Gulf Stream and near-shore stations with respect to concentrations of ammonia, nitrate, temperature, salinity, oxygen, particulate carbon, and DOC. There was a slight increase in concentration levels for propane (about 30% higher) at the near-shore station. All other parameters, methane, CO, ethane, ethylene, propylene, chlorophyll a, ^{14}carbon fixation, total phytoplankton, and pennate and centric diatoms have concentration factors R varying from 2.5 to 17.8. It is evident from these preliminary data that biological processes have a direct influence on the production of light hydrocarbons and carbon monoxide. Data obtained in this field study yield at least a qualitative picture with a casual cause-effect relationship. One should bear in mind that many parameters that can greatly affect the results, for example, levels of illumination and bacterial activity, were not monitored. More definitive experiments are being considered.

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